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(54) Preparation of 1,2-diacyl-2-(t-alkyl)hydrazines.

(57) The present invention provides a process for preparing 1,2-diacyl-2-(*t*-alkyl)hydrazines. More particularly, the present invention a process for preparing the aforesaid diacylhydrazines utilizing a solvent comprising an ester or a mixture of an ester and water in a process wherein an aromatic acid chloride is reacted in a first step with a *t*-alkylhydrazine or a corresponding acid addition salt of a *t*-alkylhydrazine such as the hydrochloride salt in the presence of a base to afford a 1-acyl-2-*t*-alkylhydrazine followed by a second step wherein an aromatic acid chloride is reacted with the aforesaid monoacylhydrazine in the presence of a base to afford the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine. Such compounds are known to have excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

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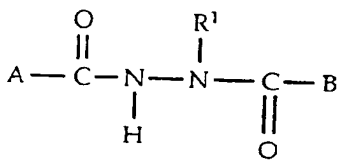
The present invention is concerned with a process for preparing 1,2-diacyl-2-(*t*-alkyl)hydrazines. More particularly, the present invention is concerned with a process for preparing the aforesaid diacylhydrazines, utilizing a solvent comprsing an ester or a mixture of an ester and water, and in which process an aromatic acid chloride is reacted in a first step with a *t*-alkylhydrazine or a corresponding acid addition salt of a *t*-alkylhydrazine such as the hydrochloride salt or the like in the presence of a base to afford a 1-acyl-2-*t*-alkylhydrazine followed by a second step wherein another aromatic acid chloride is reacted with the aforesaid monoacylhydrazine in the presence of a base to afford the desired 1,2-diacyl-2-(*t*-alkyl)hydrazine. Such compounds are known to have excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

The search for process solvents which are environmentally friendly, which are easily removed from the desired product, which provide good selectivity to the desired intermediates and products, which are easily recovered from the desired products, which allow a facile purification of the desired products, which possess favorable solubility properties for both the reactants and the desired intermediates and products, which can be used in all steps of the process, which are inert to the reaction conditions and which possess favorable process economics is a continuing one because of the difficulty in finding solvents or mixtures of solvents which fulfill all these important conditions. For example, US-A-4,985,461 discloses a process leading to 1,2-diacyl-2-(*t*-alkyl)hydrazines which employs one or more solvents such as water, alcohols such as methanol, ethanol, isopropanol and the like, hydrocarbons such as toluene, xylene, hexane, heptane and the like, glyme, tetrahydrofuran, acetonitrile, pyridine, haloalkanes such as methylene chloride or mixtures of these solvents. However, all these solvents suffer from one or more of the deficiencies previously noted. For example, water by itself results in poor intermediate and product yields and poor selectivity with a large amount of diacylation of the *t*-butylhydrazine occurring in the first process step. Alcohols such as methanol, ethanol, isopropanol and the like react with the acid chlorides, thus resulting in undesirable consumption of the acid chlorides and complicating the recovery and recycle of the process solvents. Hydrocarbons such as toluene, xylene, hexane, heptane and the like provide poor reaction selectivity in the first process step with resultant unacceptable levels of the wrong acylation isomer; additionally, these solvents are carefully regulated by governmental authorities because of environmental and safety concerns. Glyme and tetrahydrofuran are both ethers which can form undesirable levels of dangerous peroxides upon continued recovery and recycle to the process; they are also quite water soluble which further increases the difficulty of their recovery. Acetonitrile and pyridine not only are both very water soluble and hence difficult to recover in an aqueous system, but also both possess toxicological and safety concerns. Haloalkanes such as methylene chloride have a high vapor pressure which results in difficulty to contain and prevent emissions to the environment; the solubility of usual monoacylhydrazine intermediates and diacylhydrazine products is also usually very high in such solvents which results in problems to recover the aforesaid intermediates and products efficiently from such solvents.

It is, therefore, an aim of the present invention to provide a solvent which can be used in both steps of the process leading to 1,2-diacyl-2-(*t*-alkyl)hydrazines, which is environmentally friendly, which provides good selectivity, purities and yields for the aforesaid intermediates and products, which is easily recovered and recycled in the process, which allows facile removal of the product after completion of the reactions leading to it, which does not participate in the reaction process to provide undesirable side products, and which is economical to utilize. It has now unexpectedly been found that esters, more particularly aliphatic esters, possess these desirable attributes. Although US-A-4,985,461 teaches the use of the solvents listed previously, it does not teach or suggest the use of esters, with their attendant advantages, as solvents in a process to make 1,2-diacyl-2-(*t*-alkyl)hydrazines.

According to the present invention, there is provided a process, utilizing a solvent comprising an ester or a mixture of an ester and water, for the preparation at a temperature of from -20° C to 100° C of pesticidal 1,2-diacyl-2-(*t*-alkyl)hydrazine compounds of the formula



wherein

R^1 is a tertiary (C_4-C_8)alkyl group,

A and B are each independently (i) phenyl, (ii) naphthyl, or (iii) phenyl or naphthyl substituted with one to three of the same or different substituents selected from the group consisting of: halo; cyano; nitro; hydroxy;